Ultrafast Electron Crystallography: Principles and Applications

Thesis by

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To my parents and my wife Yen-Yu

Acknowledgement

Surely God is my help;
the Lord is the one who sustains me.
Psalms 54:4

Words cannot express my deepest thankfulness to God. I simply could not dismiss His constant guidance through various people as merely a long series of lucky incidences, as I reflect on how I have reached this far into the field of scientific research, all the way beginning from the change of my major from mathematics to chemistry and then the incorporation of physics, to the decision-making process of my coming to Caltech, to my entering Dr. Ahmed Zewail's group and then switching to the current research direction, with the spiritual support for me to hold on this path and, finally, to the result of many previous publications and the formation of this thesis. Special thanks must be given to my teacher Pastor Jeong, who has been teaching me about God and the meaning of life.

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During my 5 years of developing UEC, I was truly fortunate to have the opportunities to work with many talented scientists: chronologically, Dr. Nuh Gedik for the studies of interfacial water assemblies, prototype semiconducting materials and a superconductor thin film; Dr. Peter Baum for the investigation of transient structures during phase transformations; Dr. Jau Tang for theoretical modeling of the interfacial structural dynamics; Dr. Fabrizio Carbone for the studies of graphite and high-temperature superconductors; and Dr. Changshi Lao for the study of semiconducting nanowire materials. The instrumental advance made by Dr. Baum should be specially acknowledged because it is now an essential part of the UEC apparatus, and has enabled many new discoveries that require a femtosecond temporal resolution. In addition to these direct collaborators, I also benefited a great deal from the inspiring conversations and interactions with my colleagues that came from various different training backgrounds in Dr. Zewail's group.

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Abstract

During the last 20 to 30 years, the development and application of time-resolved experimental techniques with a femtosecond temporal resolution have brought to us much knowledge about the fundamental processes in physics, chemistry and biology. Nevertheless, standard spectroscopic methods have their limitation in the determination of the transient structures during ultrafast dynamics at the atomic level, because the spatial resolution is restricted by the wavelength of the probe pulse used. In contract, with the scheme of femtosecond optical initiation and electron probing and through the diffraction phenomenon, ultrafast electron crystallography (UEC) was recently developed as a time-resolved structure-probing technique for condensed-matter studies. The short wavelength and small pulse duration of the highly accelerated electrons used provide the atomic-scale spatiotemporal resolution. In addition, the large electron–matter interaction enables the detection of small transient changes as well as the investigation of surface and interfacial phenomena.

This thesis describes the principles of UEC and its applications to a variety of systems, ranging from nanometer-scale structures to highly correlated materials and to interfacial assemblies. By using a prototype semiconducting material, we elucidated the fundamental processes at work in different parts of the femtosecond-to-nanosecond time range; this investigation led to a conceptual change from the consideration of laser-induced heating to the examination of nonequilibrium structural modifications as a result of the transient dynamical changes in, e.g., carriers, the crystal potential, and phonons. On the basis of such an understanding, we observed and understood the colossal unidirectional expansion induced by the photoexcitation of nanostructures to be a

potential-driven result rather than a thermal one.

For highly correlated materials, we showed the effectiveness of UEC in resolving the transient intermediate structures during phase transformations as well as identifying new phases in the nonequilibrium state. An important breakthrough made by UEC was the confirmation of the anisotropic involvement of lattice in the electron pairing mechanism for high-temperature superconductors. In interfacial assemblies, we also found a nonequilibrium phase transformation in water and the phenomenon of ultrafast annealing for a better order in a self-assembled monolayer. With these successful experiences, we expect more condensed-matter studies by UEC to come.

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